Applied Mechanics and Materials Vols. 105-107 (2012) pp 1653-1656
Online available since 2011/Sep/27 at www.scientific.net
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doi:10.4028/www.scientific.net/AMM.105-107.1653

Effect of Immersion Time on Corrosion Resistance of Phytic Acid Coatings on AZ91D-Mg Alloy

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Keywords: Magnesium Alloy, Phytic Acid, Coating, Corrosion Resistance, Polarization, EIS

Abstract. Phytic acid coatings were formed on AZ91D-Mg alloy during immersion in 5.0 g/L phytic acid solution for different time. The corrosion resistance of the bare and coated samples was investigated using Tafel polarization and Electrochemical Impedance Spectroscopy (EIS) methods, and the corresponding electrochemical corrosion parameters were analyzed. The results show that the anodic and cathodic corrosion processes of AZ91D-Mg alloy are conspicuously inhibited with phytic acid coatings; the overall corrosion resistance index of AZ91D-Mg alloy is increased with immersion time; and the corrosion protection efficiency of phytic acid coatings is up to 97.8%.

Introduction

Due to low density, specific strength and stiffness, excellent castability, machine ability, and the lightest structural metal materials, magnesium alloy has been widely used in aerospace, automobile fields, biomedical, structural components, and so on[1,2]. However, the relatively corrosion resistance of magnesium alloy is poor which limits their extensive application in many fields[3,4].

Phytic acid ($C_6H_{18}O_{24}P_6$) is an innoxious organic compound, and it consists of 24 oxygen atoms, 12 hydroxyl groups and 6 phosphate carboxyl groups[2,5]. Phytic acid is a rare multi-tooth metal chelator. Recently, phytic acid has been used to inhibit the corrosion of the metals, and phytic acid coatings on the surface of magnesium alloys[2,5,6], zinc[7] and copper[8] have also been preliminary studied. But the influence of immersion time on corrosion resistance of magnesium alloys is unknown. In this study, AZ91D-Mg alloy were immersed in phytic acid solution for different time and the corrosion behavior was investigated.

Experimental

AZ91D-Mg alloy (10 mm × 10 mm × 0.2 mm) was the substrate material. Prior to phytic acid treatment, one-side of the sample was welded with copper conductor; except the side of 10 mm × 10 mm and without welding, other sides of the sample were mounted with insulated plastomer; the exposed side was polished with water-proof SiC paper no. 200, 400, 800, 1200 and 1400 grits in turn, washed in acetone, rinsed with distilled water, and dried. The AZ91D-Mg sample was obtained. The above sample was then immersed in phytic acid solution for different time, and phytic acid coatings are thus formed on AZ91D-Mg sample. The concentration of phytic acid was 5.0 g/L, and pH was 3.0 and was adjusted with NaOH. The purity of phytic acid is higher than 70%, others are analytical reagent, and all solutions were prepared with distilled water.

Tafel polarization and EIS measurements were carried out using electrochemical workstation (Model: CHI760D) with a conventional three-electrode cell system. A Saturated Calomel Electrode (SCE) was used as a reference electrode, and a platinum electrode was served as an auxiliary electrode. The bare and coated AZ91D-Mg alloy was the working electrode. Before electrochemical measurements, the sample was immersed in 3.5% NaCl solution at room temperature for 10 min to obtain a steady potential. The scan rate for polarization was 1 mV/s. EIS measurements were performed at corrosion potential in a frequency range between 100 kHz and 0.01 Hz with a potential sine signal of 10 mV. The EIS diagrams were analyzed and fitted using Zview software.

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Results and Discussion

Tafel Polarization Curves. Fig. 1 shows the Tafel polarization curves of the bare and coated AZ91D-Mg alloy after immersion in 3.5% NaCl solution. And the corresponding corrosion current density i_{cor} and corrosion protection efficiency P_{e} were listed in Table 1. P_{e} of phytic acid coatings for AZ91D-Mg alloy immersed in 3.5% NaCl solution is obtained using the expression as[9]: $P_{\text{e}}[\%] = (1 - {i_{\text{cor}}}/{i^0_{\text{cor}}}) \times 100$, where i^0_{cor} and i_{cor} are the corrosion current densities of the bare and coated AZ91D-Mg alloy, respectively (Table 1).

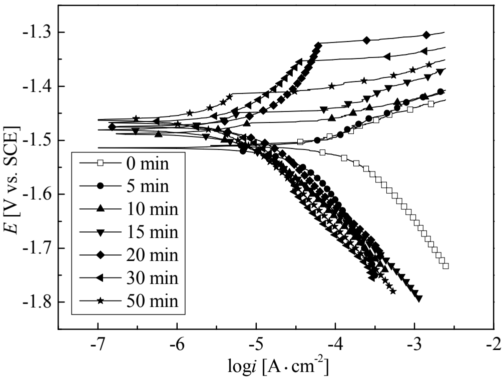

Fig. 1 Tafel polarization curves of AZ91D-Mg alloy. Immersion time was different.

Table 1 Changes of i_{cor} and P_{e} of AZ91D-Mg alloy with immersion time

Treating time [min]	i_{cor} [μA·cm^{-2}]	P_{e} [%]
0	15.09	-
5	2.27	85.0
10	0.93	93.8
15	0.51	96.2
20	0.46	97.0
30	0.42	97.2
50	0.33	97.8

As shown in Fig. 1, when AZ91D-Mg alloy was immersed in phytic acid solution for different time, both the anodic and cathodic branches on Tafel polarization curves are left-shifted differently, indicating that the anodic and cathodic corrosion processes of AZ91D-Mg alloy in 3.5% NaCl were inhibited differently with phytic acid coatings. Immersion AZ91D-Mg alloy in phytic acid solution for 5 min, the left-shift magnitude of anodic polarization branch is very small, while the cathodic polarization branch is left-shifted greatly, for about one order of magnitude. This suggests that the phytic acid coatings obtained at 5 min can effectively inhibit the cathodic corrosion process of magnesium alloy, but the inhibition degree of the anodic corrosion process is small. Lengthening immersion time to 10 min, the cathodic polarization branch is left-shifted slightly, but the anodic one is left-shifted continuously. It indicates that phytic acid coatings obtained at 10 min are more effective to inhibit both the anodic and cathodic corrosion processes of AZ91D-Mg alloy. With an increase of immersion time from 15 min to 50 min, the shift of the cathodic polarization branch is small, but the anodic one is left-shifted gradually. It can be considered that the corrosion resistance of AZ91D-Mg alloy is enhanced for a longer immersion in phytic acid solution.

As shown in Table 1, with an increase of immersion time, i_{cor} of AZ91D-Mg alloy is decreased and P_{e} is increased greatly. That is, the corrosion resistance index becomes more and more well for a longer immersion time. Moreover, the corrosion resistance index of the coated samples is highly better than that of the bare sample. It can be considered that phytic acid coatings can highly inhibit the corrosion of AZ91D-Mg alloy, where i_{cor} is decreased from 15.09 μA·cm^{-2} to 0.33 μA·cm^{-2}, for about two orders of magnitude and the corrosion protection efficiency is up to 97.8%.

EIS Diagrams. Fig. 2 shows the EIS diagrams of the bare and coated AZ91D-Mg alloy immersed in 3.5% NaCl solution. As shown in Fig. 2, the size of the diagrams for all samples is increased with immersion time, indicating an increase in impedance value of AZ91D-Mg alloy, but the shape of them is identical. These diagrams are composed of one high frequency capacitive loop (HFCL) and one low frequency capacitive loop (LFCL). HFCL can be ascribed to the corrosion products or oxides for the bare sample and the phytic acid coatings for the coated samples; LFCL can be attributed to the electric double-layer capacitance of the interface of solution/metal.

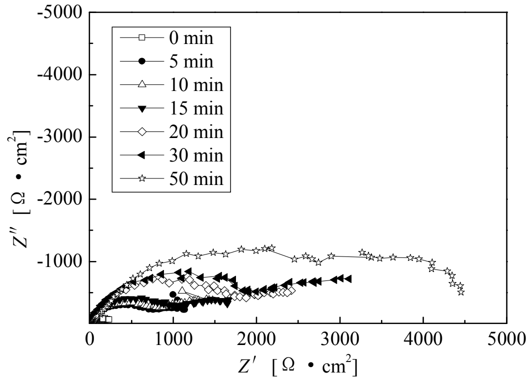

Fig. 2 EIS diagrams of AZ91D-Mg alloy treated in phytic acid solution for different time

The EIS diagrams in Fig. 2 can be described by the equivalent circuit shown in Fig. 3. R_s is the solution resistance, CPE_c is the HFCL capacitance and R_c is the resistance of the layer or coatings; CPE_{dl} is the electric double-layer capacitance and R_{ct} is the charge transfer resistance. Comparing with the pure capacitance, the frequency response characteristics of the capacitance in practical electrochemical system is deviated, which is manifested as the depression of the semicircle in Nyquist diagram[10,11]. And a constant-phase element of CPE is used to characterize the practical capacitance. CPE has an impedance dispersion relation of $Q=1/Y_0(j\omega)^n$, where n can be expressed as $n=1-2\alpha/180$, α is the depression angle of the semicircle. If n=1, 0 or −1, CPE represents a capacitance (C), a resistance (R) or an inductance (L), respectively. When $0<n<1$, CPE is denoted as the dispersion of the capacitance.

Fig. 4 shows the experimental and fitted diagrams of the coated AZ91D-Mg alloy. It is found that the fitted curve follow well with the experimental one, and the fitting error is less than 10%. Thus the proposed equivalent circuit model is feasible.

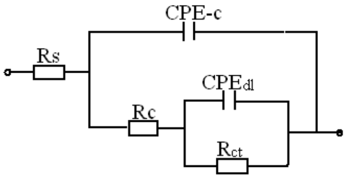

Fig. 3 Equivalent circuit used to analyzing the EIS diagrams of AZ91D-Mg alloy

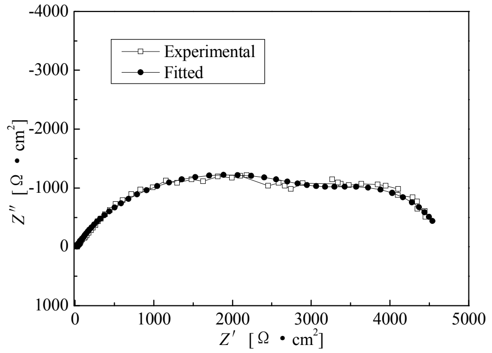

Fig.4 Comparison of the experimental and fitted diagrams

Table 2 lists the EIS fitted parameters of Y_0-CPEc, n-CPEc and R_c at HFCL of AZ91D-Mg alloy. n-CPEc is in the range of 0.7< n-CPEc <1, and it is increased with immersion time up to 30 min but it is decreased after immersion for 50 min. Benedetti[12] found that the smoother and clearer the electrode surface is, the larger the n value is. Thus phytic acid coatings on AZ91D-Mg alloy become more and more compact and complete after immersion for 30 min. Y_0-CPEc is decreased with an increase in immersion time up to 30 min but it increases for a longer time. Y_0-CPEc is related to the electrical conductivity of the coatings; the smaller Y_0-CPEc is, the more difficult of the conductivity of the coatings is. Moreover, R_c is increased with immersion time up to 50 min. In accordance with the results of Tafel polarization measurements, it can be considered that the overall corrosion resistance index of phytic acid coatings on AZ91D-Mg alloy is enhanced with an increased in immersion time up to 50 min and is superior to that of the bare sample.

Table 2 EIS fitted parameters of Y_0-CPEc, n_0-CPEc and R_c of phytic acid coatings at HFCL

Treating time [min]	Y_0-CPEc [$\Omega^{-1}\cdot cm^{-2}\cdot s^{-n}$]	n-CPEc	R_c [$\Omega\cdot cm^2$]
0	6.982×10^5	0.892	116
5	1.820×10^5	0.915	721
10	1.146×10^5	0.948	786
15	1.000×10^5	0.952	942
20	0.656×10^5	0.958	1582
30	0.621×10^5	0.967	1760
50	1.960×10^5	0.732	3722

Conclusions

1) The anodic and cathodic processes of the corrosion of AZ91D-Mg alloy in 3.5%NaCl solution are inhibited greatly with phytic acid coatings; the corrosion current density is decreased from 15.09 $\mu A\cdot cm^{-2}$ to 0.33 $\mu A\cdot cm^{-2}$, and the corrosion protection efficiency of phytic acid coatings is up to 97.8%.

2) Phytic acid coatings on AZ91D-Mg alloy become more and more compact and complete with an increase in immersion time up to 30 min, and the resistance of phytic acid coatings and the impedance of AZ91D-Mg alloy are also increased with treating time up to 50 min.

3) Phytic acid coatings markedly enhance the corrosion resistance of AZ91D-Mg alloy.

Acknowledgments

This work was supported by the Scientific Research Project of Xiamen University of Technology (No.YKJ10021R), National Nature Science Foundation of China (No. 50908091), Nature Science Foundation of Fujian Province (No. 2009J01256), and Fundamental Research Funds for the Central Universities of Huaqiao University (JB-SJ1011).

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10.4028/www.scientific.net/AMM.105-107

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